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Density Studies in Terephthalylidene-BIS-*p*-n-Decylaniline

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The temperature dependence of density in terephthalylidene-*p*-n-decylaniline (TBAA10) is carried out to probe the phase transitions, associated volume jumps, order of the transitions, and to estimate the pressure dependence of transition temperatures and pretransitional effects. The compound exhibits smectic A, smectic C, smectic I, smectic F and smectic G phases. The isotropic–smectic A and smectic C–smectic I phase transitions are found to be first order and the calculated thermal expansion coefficient also supported the density results. The smectic A–smectic C and for the first time smectic I–smectic F transitions are detectable by density changes. The calculated pressure estimate of transition temperatures from the density–enthalpy data and volume changes associated with the phase transitions are compared with the reported *P–T* data using metabolemeter. The observed two phase coexistence of the smectic A-isotropic and smectic A–smectic C phases in the vicinity of the phase transitions is compatible with reported results. The volume jumps associated with the smectic A—isotropic transition in other compounds are also presented.

Keywords: phase transitions, density, order of the phase transitions, TBAA (10)

INTRODUCTION

One of the most interesting homologous series exhibiting varied polymesomorphism is terephthalylidene bis-(*p*-n-alkyl anilines) in the last decade.[1–4] Several interesting studies have been carried out in

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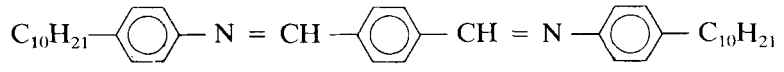
this homologous series viz., the specific identification of the smectic G and H phases in a single compound,[5] the smectic F and smectic I phases, two or three second order S_A-S_C, S_I-S_F and S_F-S_G phase transitions in addition to first order transitions etc. The phase transition studies in this homologous series, which gained prominence in recent years, however mainly confined to thermal microscopy,[1,2] x-ray investigations,[3,6,7] differential scanning calorimetry and high pressure studies[8,9] by differential thermal analysis and thermal microscopy. The decyl homologue terephthalylidene bis (*p*-n-decylaniline) exhibits an uncommon phase sequence of smectic A, smectic C, smectic I, smectic F and smectic G phases. Buisine[8] reported the phase behaviour of the above compound using a metabolemeter which inferred the order of the phase transitions, Clapeyron slopes and pressure dependence of transition temperatures. Wiegeleben *et al.*[2] reported noticeable heat of transition at the smectic A—smectic C transition. Gane *et al.*[10] studied interlayer molecular correlations and other structural relations between S_I and S_F phases. Here we report the density studies for the first time across the smectic C—smectic I and smectic I—smectic F transitions in addition to the isotropic—smectic A and smectic A—smectic C transitions in terephthalylidene bis (*p*-n-decyl aniline) (hereafter referred as TBDA).

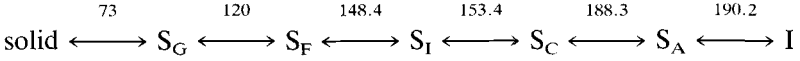
EXPERIMENTAL

The densities were carried out with a bicapillary pyknometer containing a sample of approximately 3 ml. The experimental details are described elsewhere.[11,12]

The sample was prepared by condensation of *p*-n-decylaniline (0.2 mole) and terephthaldehyde (0.1 mole) in refluxing absolute ethanol in the presence of a few drops of glacial acetic acid. After refluxing the reactants for four hours the solvent was removed by distillation under reduced pressure and later the pure compound was recrystallised from absolute alcohol-benzene mixture until the observed temperatures were constant. The transition temperatures were determined using a polarizing microscope. Special precautions were taken to keep the sample away from atmospheric hydrolysis since the sample has shown a tendency to decompose at high temperature because of prolonged heating. The decomposition was indicated by a change in colour, transition temperaures, widening in transition temperatures range and density values as it was observed in other homologues.[11,13]

The observed transition temperatures in °C by thermal microscopy are as follows.





RESULTS AND DISCUSSION

The results of the density variation with temperature in TBDA in the isotropic, smectic A, smectic C, smectic I and smectic F phases are illustrated in Figures 1 and 2. The density in all the phases excluding the vicinity of transition regions, increases with the decreasing temperature. No hysteresis was observed in density in the heating and cooling cycles in isotropic, smectic A and smectic C phases. The isotropic—smectic A transition is inferred with a significant jump in density. Further coexistence of isotropic and smectic A phases is observed for 0.6°C. This is also observed at different cooling rates and with different purified samples. However significant jump in density at the transition is completed within 0.2°C. The observed density jump across the transition is 1.82% and is in agreement with the reported values[14,15] across this transition. The minimum[14] and maximum[15] values of density change ($\Delta\rho/\rho$) reported so far across S_A-I transition are 0.35% and 2% respectively. In compounds exhibiting two phase transitions separated by a narrow temperature range, large density jumps are observed in some compounds at the phase transition on the high temperature side. In the present case also the compound exhibits S_A phase for 2°C above S_C and a large density jump of $\Delta\rho/\rho = 1.82\%$ is observed at the S_A-I transition. Analogous results are observed[14,16] at the nematic-smectic *A* transition in the compounds exhibiting narrow nematic phase.

The estimated thermal expansion coefficient ($\alpha = d\ln V/dT$) where V = molar volume is illustrated in Figure 3. An estimate of the pressure dependence of transition temperatures can be given using the Clausius-Clapeyron equation $(dT_t/dP) = T_t(\Delta V/\Delta H)$ where T_t is transition temperature, ΔV is the molar volume change associated with the transition and ΔH is the heat of transition. The estimated values of the pressure dependent transition temperatures and the

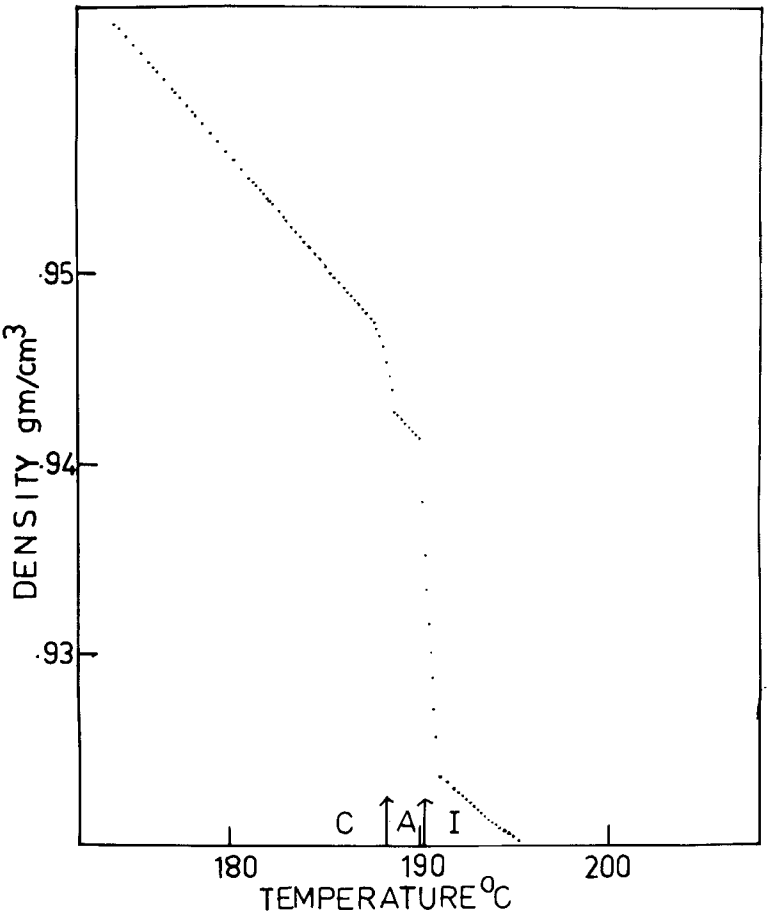


FIGURE 1 Density variation with temperature in isotropic, smectic A and smectic C phases.

molar volume changes are presented in Table I. The estimated value of pressure dependent transition temperature from the molar volume change and heat of transition ($(dT_t/dP) = 72.2$) is found to be higher than the experimental value[8] (55.5). This discrepancy may be due to the value of ΔH. Buisine[8] reported two different values of ΔH at this transition. ΔH is dependent upon the purity of the sample. Further ΔH the enthalpy is the result of two contributions viz., heat of transition and pretransitional heat of transition. Moreover the observed volume change is more than the estimated volume change from the pressure-temperature studies.[8]

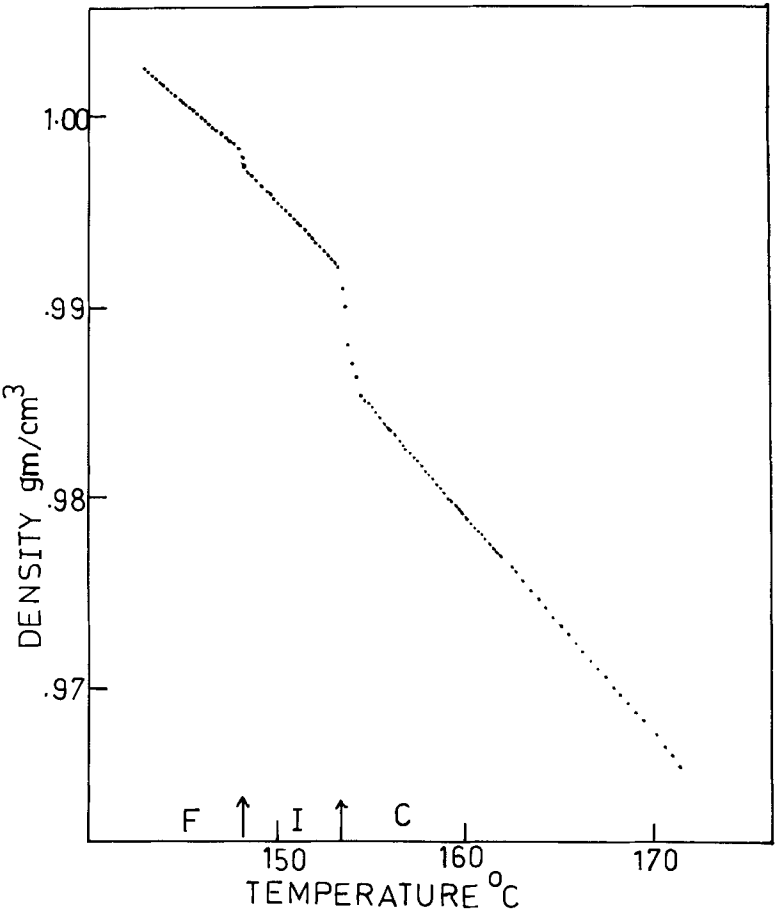


FIGURE 2 Density variation with temperature in smectic C, smectic I and smectic F phases.

The smectic A—smectic C transition is found to be different from the other liquid crystal compounds exhibiting this transition. The transition is inferred by a continuous change in density with a smeared or coexisting region of A and C phases and noticeable jump at the transition. The smeared or coexisting region is indicated by the domains of different transparency. Further the reported transition enthalpies (1770 J/mole[2], 480 J/mole[8]), which include true latent heat associated with the transition besides pretransitional heat of transition, are very much higher than the reported pretransitional heats of transition associated with other second order smectic-smectic phase

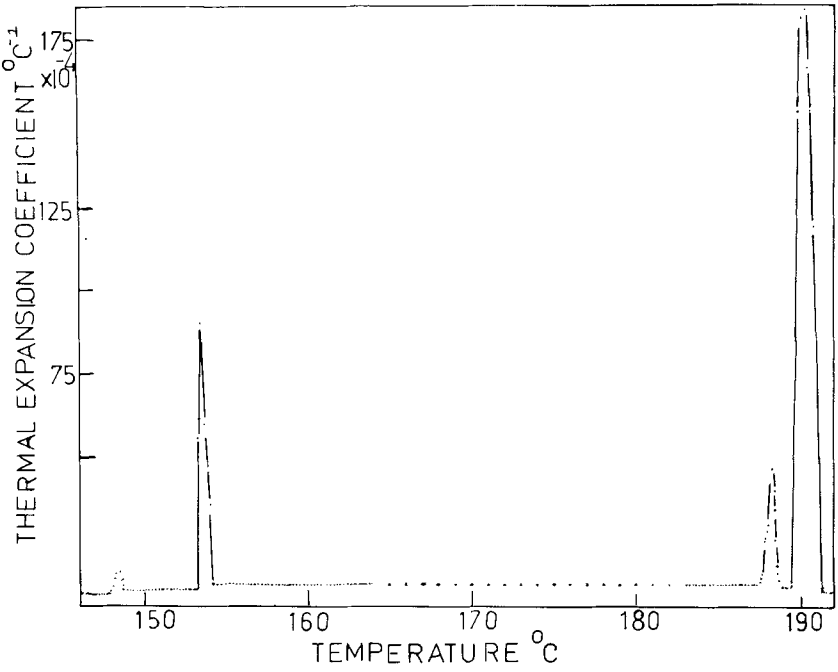


FIGURE 3 Temperature dependence of thermal expansion coefficient in TBDA.

transitions in liquid crystals. The density variation with temperature is indicated by the pretransitional effects on both sides of the transition. The thermal expansion coefficient variation also indicates the pretransitional effects. The (dT_t/dP) value (61.0 K/k bar) is however smaller than the reported value (71.4). The molar volume change which is the vertical distance between the extrapolated curves at the transition temperature is higher than the reported value.

The smectic C—smectic I transition is an example of disordered tilted structure to ordered tilted structure smectic transition. The C—I transition is found only in TBAA(A = 9) and TBAA(A = 10) homologues. We are not aware of any other report of density studies across this transition. The density jump across this transition is found to be 0.5% which do not compliment the high transition enthalpy value.[2] The thermal expansion coefficient which is higher in smectic I phase than in smectic C phase indicates the closer molecular packing in smectic I phase, leading to rigidity of molecules. Smectic I phase is shown to be essentially $2d$ phase with many weak interlayer correlations, long range ($3d$) bond orientational order and short range

TABLE I

Experimental and literature data for transition temperature, volume change at the transition, molar enthalpy change and estimated pressure dependence of transition temperatures

	I	S_A	S_C	S_I	S_F	S_G	K	Ref
Temperature	190.2	188.3	153.4	148.4	120		43	@
	190.2	188.4	154.4	148.7	115		72.2	2
Volume change	11.0	2.34	3.12					@
cm^3/mole	8.72	1.16	6.6	0.016	0.0008		40.25	8
Molar enthalpy *J*/mole	7080	1770	6310	18	2.4		50500	2
Clapeyron slope *K*/*k*. bar	72.25	61	21					@
	55.5	71.4	43.4	40	15.3		27.7	8

@Present work

positional order in the layers. Further the molecules are arranged in tilted pseudo hexagonal packing with the hexagon tilted towards an apex of the hexagon. The transition from the smectic C phase possessing one dimensional translational order of tilted molecules with fluid layers to smectic I phase is expected to be first order transition. The distinct jump in density across the C–I transition and the thermal expansion coefficient suggest a first order transition. The volume jump occurred at this transition is 3.1 cm^3/mole while the volume jump in bis-(*p'*-n-heptyloxy benzylidene) 1,4-phenylene-diamine (HBPD) is found to be 3 cm^3/mole at the C–I transition by volumetric studies.[17] From the *P-T* data,[8] the estimated volume jumps at this transition (6.6 cm^3/mole for TBDA and 1.85 cm^3/mole for HBPD) are in disagreement with the observed volume jumps. Further the pressure dependence of transition temperatures for HBPD obtained using metabolemeter and high pressure DTA studies are deviating by about 20% from one another. Hence a comparison of pressure dependence of transition temperatures estimated from the present studies and reported enthalpy data[2] with the values from *P-T* data[8] and any argument to explain the discrepancy in the volume jumps at this transition may not lead to realistic conclusions.

The smectic I–smectic F transition is an example of ordered-ordered tilted smectics transition and is indicated by a change of slope in density studies. The thermal expansion coefficient maxima at the transition temperature and its decrease with the transition from smec-

tic I into smectic F phase also indicate the transition. The lower value of thermal expansion coefficient suggests closer packing of molecules leading to further rigidity in smectic F phase than in smectic I phase. Gane *et al.*[10] described that the smectic I–smectic F transition is accompanied by a change in the direction of tilt of the pseudo hexagonal molecular packing. The important difference between the two phases being molecular arrangement in a layer. Our results are in good agreement with a change in slope of the P-T data[8] and a small value of heat of transition (18 J/mole) which may result from pretransitional effects. This transition is an example of second order transition in smectics transition.

CONCLUSIONS

The density jump at S_A-I transition is found to be in good agreement with the literature values. The S_A-S_C transition is found to be accompanied by a noticeable change in density contrary to the previous observations at this transition. This fact is supported by the reported enthalpy values. The meagre data across the smectic C–smectic I and smectic I–smectic F transitions needs further work to establish the volume jumps, order of the phase transitions and pretransitional phenomena. Further work is in progress in Terephthalylidene bis (*p*-n-dodecylaniline) (TBDDA) which also exhibits S_C, S_I, S_F and S_G phases. The volume jumps across the S_A-I transition are presented in Table II for completeness.

TABLE II

Volume jumps associated with S_A-I transition in different compounds

compound	$\Delta V/V\%$	Ref
di-*n*-hexadecyl 4,4′-azoxy cinnamate	0.4	14
di-*n*-undecyl 4,4′-azoxy cinnamate	0.35	14
di-*n*-undecyl 4,4′-azoxy α methyl cinnamate	1.21	14
n-amyl 4 (4-*n*-dodecyloxy benzylidene amino) cinnamate	1.28	14
diethyl 4,4′-azoxy dibenzoate	2.0	15
terephthalylidene bis *p*-n-octyl aniline	0.9	11
N(*p*-n-octyloxy benzylidene)*p*-n-butyl aniline	1.1	19
N(*p*-n-octyloxy benzylidene)*p*-n-octyl aniline	0.73	20
N(*p*-n-heptyloxy benzylidene)*p*-n-octyl aniline	1.04	20

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